

- 5.2 Fluoride Ion Activity Electrode, such as Orion No. 94-09⁽¹⁾.
- 5.3 Reference electrode, single junction, sleeve-type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.
- 5.4 Magnetic Mixer, Teflon-coated stirring bar.

6.0 Reagents

- 6.1 Buffer solution, pH 5.0-5.5: To approximately 500 mL of distilled water in a 1 liter beaker add 57 mL of glacial acetic acid, 58 g of sodium chloride and 4 g of CDTA⁽²⁾. Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 mL will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.
- 6.2 Sodium fluoride, stock solution: 1.0 mL = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.
- 6.3 Sodium fluoride, standard solution: 1.0 mL = 0.01 mg F. Dilute 100.0 mL of sodium fluoride stock solution (6.2) to 1000 mL with distilled water.
- 6.4 Sodium hydroxide, 5N: Dissolve 200 g sodium hydroxide in distilled water, cool and dilute to 1 liter.

7.0 Calibration

- 7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/L by diluting appropriate volumes to 50.0 mL. The following series may be used:

Millimeters of Standard (1.0 mL = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	1.60
10.00	2.00

- 7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration at the bottom of the scale.
Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8.0 Procedure

- 8.1 Place 50.0 mL of sample or standard solution and 50.0 mL of buffer (See Note) in a 150 mL beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/L on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (> 9), add 1 N HCl to adjust pH to 8.3.

9.0 Precision and Accuracy

- 9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/L fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/L with a standard deviation of ± 0.03 was obtained.
- 9.2 On the same study, a synthetic sample containing 0.75 mg/L fluoride, 2.5 mg/L polyphosphate and 300 mg/L alkalinity, was analyzed by the same 111 analysts; a mean of 0.75 mg/L fluoride with a standard deviation of ± 0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1,2-cyclohexylene dinitrilo tetraacetic acid. (The monohydrate form may also be used.) Eastman Kodak 15411, Mallinckrodt 2357, Sigma D 1383, Tridom-Fluka 32869-32870 or equivalent.
3. Standard Methods for the Examination of Water and Wastewaters, p 389, Method No. 414A, Preliminary Distillation Step (Bellack), and p 391, Method No. 414B, Electrode Method, 14th Edition (1975).
4. Annual Book of ASTM Standards, Part 31, "Water", Standard D1179-72, Method B, p 312 (1976).